

**Process for coating metallic bodies with a phosphating solution and the phosphating solution**

[0001] The present invention relates to a process for phosphating metallic bodies, in particular as a pretreatment for cold shaping, as a pretreatment for a metal-rubber composite or for adjusting coefficients of friction for connection in the case of metallic connecting elements which are finished per se.

[0002] The formation of phosphate layers on metallic objects has been used for decades with quite different compositions. These coatings primarily serve as protection from corrosion and to increase the adhesive strength of a subsequent layer, such as e.g. a lacquer layer. The phosphate layer here often typically has a layer thickness of about 2 to about 30  $\mu\text{m}$ .

[0003] For cold shaping the metallic bodies to be shaped are often coated with one to four layers of usually different composition so that the cold shaping and in particular the wire drawing, flow pressing or tube drawing can take place with a significantly reduced friction, significantly lower force, significantly less wear on the shaping body and the device, significantly reduced expenditure on time and with optimized surface qualities of the shaped bodies. A layer sequence of a phosphate layer and a soap layer, e.g. of metal stearates, is often chosen. The phosphate layer here typically has a layer thickness of about 2 to about 20  $\mu\text{m}$ . Phosphate layers based on phosphates of Zn, ZnMn, ZnCa or ZnFe are usually employed for the cold shaping.

[0004] EP 0 613 964 B1 protects a process for application of a phosphate coating, in which objects of iron-based materials are dipped by dipping in a phosphating solution containing phosphate, zinc, magnesium, fluoroborate and chlorate in certain ratios. No nitrogen-containing compounds should be added to this solution. The chlorate contents of about 3 g/l serve here both for acceleration and for oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . However, the process has the disadvantages that the phosphating bath requires comparatively high contents of zinc, magnesium, fluoroborate and chlorate, and that a relatively high pickling erosion and a large sludge volume are unavoidable. In throughput over two to three days, the sludge volume is often 300

to 500 mg/l. The average edge length of the phosphate crystals prepared with the process was at least 50  $\mu\text{m}$ .

[0005] DE 199 47 232 A1 relates to a process for application of a manganese phosphate layer to iron-containing metallic surfaces, in which zinc-free solutions with a content of  $\text{Fe}^{2+}$  ions, 10 to 25 g/l of manganese ions, phosphate ions, 3 to 35 g/l of nitrate ions and 0.5 to 5 g/l of nitroguanidine are employed.

[0006] DE 196 34 685 A1 relates to a process for phosphating metallic surfaces, in which a solution containing phosphate, zinc, nitrate and nitroguanidine is used. However, the solutions are free from additions of alkaline earth metal ions.

[0007] The doctrine of DE 38 00 835 A1 is a process for phosphating metal surfaces in which the metallic surfaces are brought into contact with a solution containing very high contents of phosphate, zinc, calcium and at least one accelerator chosen from nitrate and organic nitro compounds, without prior activation. The content of calcium and zinc should be 10 to 40 g/l.

[0008] DE 36 36 390 A1 describes a process for producing phosphate coatings on iron-containing metal surfaces in which the metallic surfaces are brought into contact with a quite high contents of phosphate, zinc, manganese, nitrate, fluoroborate and tartaric acid or/and citric acid and optionally urea, without prior activation. The content of zinc should be 5 to 25 g/l, that of nitrate 5 to 50 g/l. The disadvantages of this process lie in the fact that it is used with a very high nitrate content and without self-limitation of the dissolved  $\text{Fe}^{2+}$ .

[0009] US 4,517,029 protects a process for the treatment of iron-containing metallic surfaces with a phosphating solution which contains 5 to 30 g/l of phosphate, 1 to 15 g/l of zinc ions, 1 to 3.5 g/l of calcium ions and 30 to 50 g/l of nitrate ions.

[0010] There was therefore the object of proposing a process for phosphating surfaces of metallic objects which is suitable for forming phosphate layers for cold shaping, in which the content of sludge formed during the phosphating can be reduced noticeably, as far as possible without sacrificing profitability and industrial applicability. With the reduction in the formation of sludge, the consumption of chemicals during the phosphating is also lowered.

[0011] There was moreover the object of proposing a process for phosphating surfaces of metallic objects which is as environment-friendly as possible, so that the contents of heavy metals, nitrate, nitrite and other nitrogen-containing compounds can be kept low.

[0012] The object is achieved with a process for coating surfaces of metallic objects, in particular as a pretreatment for cold shaping or as a pretreatment for a metal-rubber composite or for adjusting the coefficients of friction of connecting elements for use of these connecting elements, such as e.g. screws for screwing, which is characterized in that the metallic objects, which are optionally already precoated, are coated with an aqueous, acidic composition containing phosphate, which comprises

[0013] 8 to 50 g/l of phosphate, calculated as  $\text{PO}_4$ ,

[0014] 0.5 to 30 g/l of zinc ions,

[0015] 0 to 5 g/l of manganese ions,

[0016] 0 to 8 g/l of calcium ions,

[0017] 0 to 5 g/l of magnesium ions,

[0018] wherein at least 0.1 g/l of calcium or/and magnesium ions are present,

[0019] 0.1 to 5 g/l of nitroguanidine,

[0020] 0.1 to 10 g/l in total of chlorate or/and peroxide ions,

[0021] in total 0 to 16 g/l of complex fluoride ( $\text{MeF}_4$  or/and  $\text{MeF}_6$ ) of  $\text{Me} = \text{B}, \text{Si}, \text{Ti}, \text{Hf}$  or/and  $\text{Zr}$  and

[0022] 0 to 5 g/l of fluoride ions,

[0023] wherein the total content of complex fluoride and fluoride ions is in the range from 0.1 to 18 g/l.

[0024] The content of phosphate is preferably 9.5 to 42 g/l, particularly preferably 11 to 34 g/l, very particularly preferably 12 to 28 g/l, in particular 13 to 22 g/l, above all at least 14 g/l or at least 15 g/l or up to 20 g/l or up to 18 g/l.

[0025] The content of zinc ions is preferably 0.8 to 24 g/l, particularly preferably 1 to 18 g/l, very particularly preferably 1.5 to 12 g/l, in particular 2 to 8 g/l. The zinc content of the composition for the cold shaping is preferably in the range from 2.5 to 28 g/l, in particular 5 to 25 g/l. In some cases the zinc content can also be lowered to values in the range of  $1.5 \pm 1$  g/l.

[0026] The content of manganese ions is preferably 0.05 to 4.5 g/l, particularly preferably 0.1 to 4 g/l, very particularly preferably 0.2 to 3 g/l, in particular 0.3 to 2 g/l. The composition according to the invention preferably contains zinc and manganese ions in a ratio of Zn : Mn in the range from 40 : 1 to 1 : 2, particularly preferably in the ratio of 30 : 1 to 1 : 1, very particularly preferably in the ratio of 20 : 1 to 1.5 : 1, in particular in the ratio of 10 : 1 to 2 : 1.

[0027] Preferably, no nickel or only a small amount of nickel is added to the composition, while some or all of the nickel content under certain circumstances can be formed by the pickling effect on a nickel-containing metal surface, since nickel belongs to the toxic and environment-unfriendly heavy metals. On the other hand, it is often advantageous to find or to add at least a low content. The composition then preferably comprises nickel ions in the range from 0.01 to 2 g/l, particularly preferably 0.05 to 1.5 g/l, very particularly preferably 0.1 to 1 g/l, in particular only up to 0.8 g/l or up to 0.5 g/l.

[0028] The composition according to the invention preferably comprises phosphate and zinc in a ratio of  $\text{PO}_4$  : Zn in the range from 40 : 1 to 1 : 1, particularly preferably in a ratio of 30 : 1 to 1.5 : 1, very particularly preferably in a ratio of 20 : 1 to 2 : 1, in particular in a ratio of 10 : 1 to 3 : 1.

[0029] The content of dissolved  $\text{Fe}^{2+}$  ions is preferably limited to contents of less than 5 g/l, particularly preferably to contents of less than 4 g/l, very particularly preferably to contents of less than 3 g/l, in particular to contents of less than 2 g/l, 1.5 g/l or 1 g/l. Above 4 g/l under certain circumstances problems arise due to the formation of coarse phosphate crystals, which lead to rough instead of smooth phosphated surfaces. In many cases it will therefore be preferable to limit the content of dissolved  $\text{Fe}^{2+}$  ions to less than 2.5 g/l or even lower, in particular in order to render possible a fine-grained layer formation with a smooth surface.

[0030] The content of calcium ions is preferably 0.05 to 6 g/l, particularly preferably 0.1 to 5 g/l, very particularly preferably 0.15 to 4 g/l, in particular up to 3 g/l, up to 2 g/l or up to 1 g/l. A content of calcium ions can help to reduce the amount of sludge formed in the bath by precipitation, can assist the formation of Ca- and Zn-containing phosphate or/and can reduce or suppress the formation of ZnFe-containing phosphate.

[0031] The content of magnesium ions is preferably 0.05 to 4 g/l, particularly preferably 0.1 to 3 g/l, very particularly preferably 0.15 to 2 g/l, in particular up to 1 g/l. A content of magnesium ions can help to form more finely grained phosphate crystals.

[0032] The composition according to the invention preferably comprises magnesium and calcium ions with a content of in each case at least 0.1 g/l or of in each case at least 0.2 g/l or/and in a ratio of Mg : Ca in the range from 40 : 1 to 1 : 2, in particular from 30 : 1 to 1 : 1.5, above all from 3 : 1 to 1 : 1. The total content of magnesium and calcium ions is preferably 0.15 to 10 g/l, particularly preferably 0.2 to 8 g/l, very particularly preferably 0.25 to 6 g/l, in particular up to 5 g/l, up to 4 g/l, up to 3 g/l or up to 2 g/l.

[0033] With an increased content of magnesium fluoride in the solution, however, the bath can come into a thixotropic gelatinous state in individual cases, due in particular to complex magnesium compounds. The addition of boric acid or/and other boron compounds can then help to lower the content of free fluoride in the bath, in order to help to avoid higher troublesome contents of complex magnesium compounds of this type.

[0034] By the content of alkaline earth metals, such as e.g. Ca, possibly in combination with nitroguanidine, the sludge can often be brought into a sludge mass which is easy to handle, soft, readily compactable and easy to rinse off. As a result the sludge does not become encrusted on the surfaces of the devices, such as e.g. bath container, attachments, heating installations, tanks and pipelines, and can easily be removed or taken away.

[0035] The presence of at least one complex fluoride may be advantageous in particular because of a more uniform pickling attack and may possibly also help to

form thicker phosphate layers. The total content of complex fluorides is preferably 0.1 to 6 g/l, particularly preferably 0.2 to 5 g/l, very particularly preferably 0.3 to 4 g/l, in particular up to 3 g/l, up to 2 g/l or up to 1 g/l.

[0036] The content of fluoroborate is preferably 0.1 to 5 g/l, particularly preferably 0.2 to 4 g/l, very particularly preferably 0.3 to 3 g/l, in particular up to 2 g/l or up to 1 g/l. Alternatively or in addition, a titanium or/and zirconium hexafluoride can be used in particular.

[0037] At least one complex fluoride can be advantageously added in particular if the metallic surface is more heavily contaminated by oxide deposits and is to be superficially pickled as uniformly as possible. An addition of complex fluoride can lead here to somewhat higher layer thicknesses.

[0038] The composition can preferably comprise fluoroborate, in particular in the range from 0.1 to 5 g/l, particularly preferably in the range from 0.2 to 3 g/l. An addition of fluoroborate has the advantage that it has a particularly potent pickling action. The complex fluoride is advantageously present to the extent of at least 30 wt.%, to the extent of at least 60 wt.%, to the extent of at least 80 wt.% or completely as fluoroborate.

[0039] In some cases it may be advantageous, alternatively or in addition to the content of at least one complex fluoride, to add fluoride ions e.g. in the form of hydrofluoric acid, preferably 0.05 to 2.5 g/l of fluoride ions, in particular 0.1 to 1.8 g/l, above all 0.2 to 1.5 g/l. The content of fluoride ions can preferably be in the range from 0.05 to 2.5 g/l, in particular in the range from 0.1 to 1.8 g/l, above all in the range from 0.3 to 1.5 g/l. This can be favourable in particular for the formation of thicker layers or in the case of problems in the cleaning of the metallic surfaces. A content of free fluoride, which may possibly react chemically with magnesium ions, is derived from this and to a limited extent from the complex fluoride. However, it should be checked whether troublesome effects occur in the presence of magnesium ions and fluoride ions.

[0040] The composition comprises complex fluoride or/and fluoride ions to calcium ions preferably in a ratio of ( $\text{MeF}_4$ ,  $\text{MeF}_6$  or/and  $\text{F}^-$ ) : Ca in the range from 0.1 : 1 to

10 : 1, particularly preferably in the range from 0.3 : 1 to 8 : 1, very particularly preferably in the range from 0.5 : 1 to 6 : 1.

[0041] The composition comprises complex fluoride or/and fluoride ions to magnesium ions preferably in a ratio of ( $\text{MeF}_4$ ,  $\text{MeF}_6$  or/and  $\text{F}^-$ ) : Mg in the range from 0.1 : 1 to 10 : 1, particularly preferably in the range from 0.2 : 1 to 6 : 1, very particularly preferably in the range from 0.3 : 1 to 4 : 1.

[0042] Nitroguanidine and corresponding N-containing guanidine compounds serve in particular as accelerators in order to depolarize the hydrogen, as a result of which nitroguanidine can be converted into aminoguanidine. Aminoguanidine is readily biodegradable and non-toxic. However, the nitroguanidine additionally also seems to passivate the surface well. The content of nitroguanidine is preferably 0.15 to 4.5 g/l, particularly preferably 0.2 to 4 g/l, very particularly preferably 0.25 to 3 g/l, in particular 0.3 to 2.5 g/l, above all up to 2 g/l or up to 1.5 g/l.

[0043] Although they are often called accelerators, N-containing guanidine compounds evidently do not act as accelerators, since they apparently do not oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , but act rather as passivating agents. They therefore differ considerably from the typical accelerators such as are employed for phosphating.

[0044] The composition preferably comprises not more than 1 g/l nitrate, calculated as  $\text{NO}_3$ , particularly preferably 0.1 to 0.8 g/l nitrate, in particular 0.3 to 0.6 g/l nitrate, or is largely or completely free from nitrate. It preferably comprises not more than 0.5 g/l of nitrite, calculated as  $\text{NO}_2$ , or is largely or completely free from nitrite. A low or very low nitrite content, often less than 0.2 g/l, may possibly form from the nitrate content. The lower the content of nitrate and nitrite in the phosphating solution, the less the waste waters which are formed during the phosphating are polluted.

[0045] Preferably no further N-containing accelerators in addition to guanidine compounds and optionally in addition to nitrate or/and nitrite are added to the aqueous composition. Alternatively, this comprises only comparatively low contents of further N-containing accelerators in addition to those just mentioned. It is advantageous here if the contents of nitrate, nitrite and NBS ions (nitrobenzenesulfonate, in particular with sodium) are in each case less than 0.8 g/l

or less than 0.4 g/l or even less than 0.2 g/l or/and the total content of all N-containing accelerators, with the exception of nitroguanidine and related guanidine compounds, such as e.g. aminoguanidine, is below 2 g/l.

[0046] Preferably, no chloride or only a small amount of chloride is added, while the predominant chloride content in many cases is formed from chlorate. The composition preferably comprises chloride ions in the range from 0.05 to 5 g/l, particularly preferably 0.1 to 4.5 g/l, very particularly preferably 0.2 to 4 g/l, extremely preferably 0.25 to 3 g/l, in particular 0.3 to 2.5 g/l, above all up to 2 g/l or up to 1.5 g/l. A content of chloride provides an additional pickling effect.

[0047] Chlorate serves above all or exclusively as an oxidizing agent to limit the content of  $\text{Fe}^{2+}$  dissolved in the aqueous composition by accelerating the precipitation to  $\text{Fe}^{3+}$ . The chlorate content can help working on the iron side, so that an increased, limitable content of  $\text{Fe}^{2+}$  remains dissolved in the bath instead of being precipitated as  $\text{Fe}^{3+}$ . It serves here as an accelerator to only a minor degree, if at all. The content of chlorate is preferably 0.15 to 7 g/l, particularly preferably 0.2 to 5 g/l, very particularly preferably 0.25 to 4 g/l, in particular up to 3 g/l, up to 2.2 g/l or up to 1.5 g/l. Above all, it is preferable to keep the chlorate content in the range from 0.8 to 2.5 g/l or even in the range from 1 to 2 g/l. On the basis of this, it may be advantageous to increase the chlorate content somewhat and approximately to the extent necessary for oxidation of the  $\text{Fe}^{2+}$  in the phosphating bath, in order to achieve a rapid precipitation and to limit the content of  $\text{Fe}^{2+}$  in the phosphating bath, e.g. if the throughput is increased.

[0048] Preferably, no sulfate is added. However, sulfate or/and chloride can be introduced in particular because of being carried along from the pickling bath, it being possible under certain circumstances for up to approx. 3 g/l to be carried in. A certain sulfate or/and chloride content may originate here from the water employed, from other impurities and from material carried in. The chlorate content present in the bath forms a content of chloride in the bath composition. If the metallic objects that are to be phosphated are not so severely contaminated and rusted, the contents of chloride or/and sulfate may be sufficient for the required pickling action in the phosphating bath, so that a pickling bath before the phosphating can be omitted. In



this case it may sometimes be advisable to add a low content of chloride or/and sulfate, in particular of in each case up to 1 g/l, to the bath.

[0049] The composition can comprise sulfate ions preferably in the range from 0.05 to 2 g/l, particularly preferably 0.1 to 1.8 g/l, very particularly preferably 0.15 to 1.6 g/l, extremely preferably 0.2 to 1.2 g/l, in particular 0.25 to 1 g/l, above all up to 0.8 g/l or up to 0.6 g/l.

[0050] The content of peroxide is preferably 0.005 to 3.5 g/l, particularly preferably 0.01 to 2 g/l, very particularly preferably 0.02 to 1 g/l, in particular 0.03 to 0.5 g/l, above all up to 0.2 g/l or up to 0.1 g/l. Peroxide can serve to limit the  $\text{Fe}^{2+}$  content in the phosphating solution and as an accelerator.

[0051] The composition can moreover comprise, in particular, a content of alkali metal or/and ammonium ions, in particular by an addition of compounds of potassium or/and sodium, such as e.g. sodium chlorate.

[0052] A content of at least one pickling inhibitor, preferably 0.005 to 0.8 g/l, particularly preferably 0.01 to 0.6 g/l, very particularly preferably 0.015 to 0.4 g/l of all pickling inhibitors, can furthermore optionally be added to the bath solution according to the invention. The content of individual pickling inhibitor is preferably in the range from 0.005 to 0.6 g/l, particularly preferably 0.01 to 0.5 g/l, very particularly preferably 0.015 to 0.4 g/l. In contrast to this, the concentrate can in each case contain the same lower limits as stated here for the bath solution, but twice the upper limits as in the bath solution. In particular, in each case at least one amide, amine, imide or/and imine, for example dimethylaminopropylamine, can be added as pickling inhibitors. Such an addition is advantageous in particular for lowering the consumption of the at least one guanidine compound.

[0053] The phosphating solution according to the invention can have, in particular, one of the following compositions:

[0054] A) 8 to 30 g/l of phosphate, calculated as  $\text{PO}_4$ ,

[0055] 0.5 to 4.5 g/l of zinc ions,

[0056] 0 to 4 g/l of manganese ions,

- [0057] 0 to 8 g/l of calcium ions,
- [0058] 0 to 5 g/l of magnesium ions,
- [0059] wherein at least 0.1 g/l of calcium or/and magnesium ions are present,
- [0060] 0.1 to 5 g/l of nitroguanidine,
- [0061] 0.1 to 8 g/l in total of chlorate or/and peroxide ions,
- [0062] in total 0 to 6 g/l of complex fluoride ( $\text{MeF}_4$  and  $\text{MeF}_6$ ) of  $\text{Me} = \text{B}, \text{Si}, \text{Ti}, \text{Hf}$  or/and  $\text{Zr}$ , wherein a content of fluoroborate is present, and
- [0063] 0 to 4 g/l of fluoride ions
- [0064] or B) 8 to 30 g/l of phosphate, calculated as  $\text{PO}_4$ ,
- [0065] 0.5 to 8 g/l of zinc ions,
- [0066] 0 to 5 g/l of manganese ions,
- [0067] 0.1 to 8 g/l of calcium ions,
- [0068] 0 to 5 g/l of magnesium ions,
- [0069] 0.1 to 5 g/l of nitroguanidine,
- [0070] 0.1 to 8 g/l in total of chlorate or/and peroxide ions,
- [0071] in total 0 to 6 g/l of complex fluoride ( $\text{MeF}_4$  and  $\text{MeF}_6$ ) of  $\text{Me} = \text{B}, \text{Si}, \text{Ti}, \text{Hf}$  or/and  $\text{Zr}$ , wherein a content of fluoroborate is present, and
- [0072] 0 to 4 g/l of fluoride ions.
- [0073] Higher contents of heavy metals should as far as possible be avoided for environmental protection reasons. Furthermore, higher contents of Al, Cr and Pb as a rule interfere with the phosphating. The phosphating solution according to the invention is advantageously substantially free or free from contents of Al, Cd, Co, Cr, Cu, Mo, V or/and W. For environmental protection reasons, the contents of nitrogen-containing accelerators, apart from nitroguanidine, should be kept as low as

possible, that is to say in particular the contents of nitrate and nitrite. Preferably, substantially no or no other nitrogen compound apart from at least one guanidine compound is added.

[0074] Preferably, all the compounds present in the bath are readily soluble in water or largely or completely dissolved in water. It is particularly preferable if all the bath constituents apart from the precipitation products are readily soluble in water and are present readily dissolved in water.

[0075] The pH of the composition can advantageously be kept in the range from 0.1 to 4, particularly preferably in the range from 0.5 to 3.5, very particularly preferably in the range from 1 to 3. Any suitable substance can in principle be added to adjust the pH; in particular on the one hand e.g. zinc carbonate and on the other hand e.g. phosphoric acid are suitable. The value of the total acid is preferably in the range from 32 to 45 points, in particular 36 to 40 points, that of the free acid preferably in the range from 5 to 8 points, in particular 6 to 7 points. The ratio of the total acid to the value of the free acid, the so-called S value, is preferably in the range from 0.1 to 0.4, particularly preferably in the range from 0.14 to 0.36, very particularly preferably in the range from 0.18 to 0.32.

[0076] The total acid points number is determined here by titrating 10 ml of the phosphating solution, after dilution with water to about 50 ml, using phenolphthalein as the indicator, until the colour changes from colourless to red. The number of ml of 0.1 N sodium hydroxide solution consumed for this gives the total acid points number. Other indicators which are suitable for the titration are thymolphthalein and ortho-cresolphthalein.

[0077] The free acid points number is determined in a corresponding manner, dimethyl yellow being used as the indicator and the titration being carried out until the colour changes from pink to yellow.

[0078] The S value is defined as the ratio of free  $P_2O_5$  to the total content of  $P_2O_5$  and can be determined as the ratio of the free acid points number to the Fischer total acid points number. The Fischer total acid is determined by using the titrated sample of the free acid titration and adding to it 25 ml 30% potassium oxalate solution and approx. 15 drops of phenolphthalein, setting the titrating apparatus to

zero, as a result of which the free acid points number is subtracted, and titrating until the colour changes from yellow to red. The number of ml of 0.1 N sodium hydroxide solution consumed for this gives the Fischer total acid points number.

[0079] The temperature of the phosphating solution is preferably kept in the range from 50 to 80°C, in particular at 55 to 75°C. However, the phosphating bath can also be employed at other temperatures, such as e.g. at temperatures in the range down to about 15°C. At short flow-through times such as e.g. 10 to 30 seconds, a high concentration and a high temperature of the phosphating solution are rather advisable.

[0080] The phosphating time can be varied within wide ranges. In particular, the time the metallic surface is in contact with the phosphating solution is in the range from 1 second to 30 minutes, preferably at least 10 seconds, but in most uses at least 1 or at least 2 minutes. Wire in particular can be phosphated in a rapid flow-through, e.g. in less than 1 minute.

[0081] The phosphate layer formed with the process according to the invention preferably comprises as phosphates Zn, ZnMn, ZnFe, ZnCa or/and CaZn phosphates, in the case of a content of calcium in particular hopeite or/and scholzite.

[0082] Preferably, a phosphate layer which has a layer thickness in the range from 0.02 to 15  $\mu\text{m}$  or/and a layer weight in the range from 0.5 to 25  $\text{g/m}^2$ , particularly preferably with a layer thickness in the range from 0.05 to 13.5  $\mu\text{m}$ , very particularly preferably with a layer thickness of at least 0.08  $\mu\text{m}$ , in particular of at least 0.12  $\mu\text{m}$  or of up to 11  $\mu\text{m}$  is formed. With the composition according to the invention it is possible to form phosphate layers of exceptionally different layer thickness. On the one hand it may be advantageous e.g. for cold shaping to form phosphate layers with a layer weight in the range from 1.5 to 18  $\text{g/m}^2$  - for pipes here in particular in the range from 1.5 to 6  $\text{g/m}^2$ , for wire in particular in the range from 1.5 to 10  $\text{g/m}^2$  and in the case of cold solid shaping e.g. of bolts and discs in particular in the range from 3 to 18  $\text{g/m}^2$ . On the other hand e.g. for coating of connecting elements such as rivets and screws, phosphate layers with a layer weight in the range from 1.5 to 12  $\text{g/m}^2$  may be advantageous. If the phosphate layers are to be employed as a

pretreatment for a metal-rubber composite, it may be advantageous to form layer thicknesses with a layer weight in the range from 0.5 to 3 g/m<sup>2</sup>.

[0083] The phosphate layers that are employed according to the prior art for cold shaping typically have edge lengths of the phosphate crystals of the order of about 200 µm. In contrast, decidedly smaller phosphate crystals are formed in the process according to the invention. However, if the phosphate layers are to be finely crystalline (average edge length of the phosphate crystals about in the range from 2 to 25 µm) and as far as possible also in visual impression of approximately the same crystal size and of approximately uniform layer thickness, it may be advisable to form layer thicknesses with a layer weight in the range from 1.5 to 12 g/m<sup>2</sup>. For thick layers in particular it may be advantageous or even necessary not to form an activation layer before the phosphating, in order to establish layer thicknesses of more than 7.5 g/m<sup>2</sup>, in particular more than 10 g/m<sup>2</sup>. However, in most cases the thick phosphate layers are rather of medium to coarse crystal size, average edge lengths in the range from 25 to 300 µm often being formed - determined via the edge length of the phosphate crystals on scanning electron microscope photographs at an angle or perpendicular to the phosphated surface. The layer thicknesses and their layer weights, however, also depend on the metallic substrate chosen. Astonishingly, it was possible for even phosphate layers with a low layer weight to be shaped by cold flow pressing very well and with very low friction forces, especially if the average edge length of the phosphate crystals was less than 10 µm. As far as has been observed to date, a so-called layer-forming phosphating is evidently always carried out.

[0084] In the process according to the invention it is possible to form a phosphate layer which has an average edge length of the phosphate crystals of less than 20 µm or even of less than 10 µm and often at the same time has a layer thickness with a layer weight in the range of 1.5 to 18 g/m<sup>2</sup>, in particular in the range from 2 to 15 g/m<sup>2</sup>.

[0085] The object is also achieved with a process for coating surfaces of metallic objects with a phosphating solution, in which the ratio of pickling erosion on the metallic surface, measured in g/m<sup>2</sup>, to the layer weight of the phosphate layer, measured in g/m<sup>2</sup>, is at values below 75%, in particular below 72%, preferably

below 68%, particularly preferably below 65%, very particularly preferably below 62% or below 58%.

[0086] The phosphate layer can serve as an adhesion promoter e.g. for soaps, sliding polymers or other lubricants or corresponding mixtures which are applied subsequently to the phosphate layer and result in a lubricant layer, in particular on wires, pipes, round blanks, discs, rods or other shaped bodies for cold shaping. In numerous cases the friction cannot be reduced sufficiently for cold shaping solely with a single lubricant layer, so that at least one further lubricant layer must then also be applied. The phosphate layer can be applied e.g. to screws for screwing, so that the coefficient of friction is reduced during screwing in, in particular during automated screwing in, so that the screwing machine can be set according to the torque, which in most cases must be neither too high nor too low. The screws are predominantly screws which can be subjected to high loads.

[0087] The phosphate layer can be applied to surfaces of metallic objects such as e.g. bolts, wires, pipes, discs, rods or preshaped metallic bodies, which can optionally also have a complex geometry. The phosphate layer according to the invention is particularly suitable for precoating for a metal-rubber composite because it can also be applied very thinly - for example in the range from 0.1 to 5  $\mu\text{m}$  - and because it can be designed to be particularly firmly adhering.

[0088] All metallic materials can in principle be employed as materials which are coated on the surface of such objects, in particular iron-rich alloys, such as e.g. steels, galvanized steel and other zinc-containing surfaces.

[0089] Before the phosphating the metallic surfaces can be subjected to alkaline or/and acid cleaning or/and acid pickling, in particular depending on the nature and degree of contamination. In between or/and thereafter, at least one rinsing step with water may be appropriate. Alternatively or in addition, the metallic surfaces can optionally be precoated at least once before the phosphating, for example with an activating solution or/and with a pretreatment composition of different chemical composition to the subsequent phosphating.

[0090] It is advantageous here if the material of the metallic surface of shaped bodies for cold shaping can be pickled readily and is pickled before the coating with

the phosphate composition according to the invention, in particular with dilute mineral acids or specific acid-rich mixtures. Alternatively, the metallic surfaces to be coated can have only little or almost no contamination, if at all, so that the pickling action of the phosphating solution alone is sufficient for the remaining cleaning of the surface.

[0091] The pickling action of the phosphating bath should in many cases rather be not very severe, in order to limit the amount of sludge formed in the phosphating bath.

[0092] In many cases it is advantageous if the metallic surfaces are activated, e.g. with a titanium-containing activation or an activation based on pyrophosphate, before the phosphating. In the process according to the invention, however, it is usually not necessary to carry out an activation. By the activation it is as a rule possible to establish an even finer phosphate grain. An average edge length of the phosphate crystals of less than 30  $\mu\text{m}$ , in particular of less than 20  $\mu\text{m}$ , particularly preferably of less than 10  $\mu\text{m}$ , of less than 5  $\mu\text{m}$  or even of less than 2.5  $\mu\text{m}$  is advantageously generated, without or with prior activation. Phosphate crystals with an average edge length of less than 2.5  $\mu\text{m}$  were achieved with a phosphating solution with a 0.2 to 0.8 g/l nitroguanidine content after prior activation.

[0093] The coating according to the invention serves in particular for preparation for cold shaping, by application of the coating according to the invention before application of a layer comprising lubricant, such as e.g. a composition based on metal stearate(s). The coating for phosphating can in principle also be used to achieve a corrosion protection or/and an adhesion promotion, that is to say in particular as treatment or as pretreatment e.g. before a subsequent lacquering. It can also serve as a pretreatment for a metal-rubber composite or for adjusting coefficients of friction on connecting elements for use of these connecting elements, such as e.g. screws for screwing.

[0094] The metallic object coated according to the invention can be used in cold shaping, for a metal-rubber composite, as a connecting element with an adjusted coefficient of friction or as an element in building construction, in vehicle construction, in apparatus construction or in machine construction.

[0095] The object is also achieved with an aqueous phosphating solution which serves as a concentrate, as a bath solution or/and as a topping-up solution and which contains

[0096] 8 to 100 g/l of phosphate, calculated as  $\text{PO}_4$ ,

[0097] 0.5 to 60 g/l of zinc ions,

[0098] 0 to 10 g/l of manganese ions,

[0099] 0 to 16 g/l of calcium ions,

[00100] 0 to 10 g/l of magnesium ions,

[00101] wherein at least 0.1 g/l of calcium or/and magnesium ions are present,

[00102] 0.05 to 10 g/l of nitroguanidine,

[00103] 0 to 2 g/l of nitrate

[00104] 0.1 to 10 g/l in total of chlorate or/and peroxide ions,

[00105] in total 0 to 16 g/l of complex fluoride ( $\text{MeF}_4$  and  $\text{MeF}_6$ ) of  $\text{Me} = \text{B}$ ,  $\text{Si}$ ,  $\text{Ti}$ ,  $\text{Hf}$  or/and  $\text{Zr}$  and

[00106] 0 to 5 g/l of fluoride ions,

[00107] wherein the total content of complex fluoride and fluoride ions is in the range from 0.1 to 18 g/l.

[00108] As a bath or/and as a topping-up solution it preferably also contains nitroguanidine, but it may be preferable for the nitroguanidine to be added separately to the concentrate, to the bath solution or/and to the topping-up solution. It may be advantageous to add all the constituents of the bath, under certain circumstances with the exception of nitroguanidine or/and peroxide, in the aqueous phosphating solution which serves as a concentrate or as a topping-up solution. If nitroguanidine or/and peroxide are contained in the aqueous phosphating solution, their content is preferably in each case at least 0.1 g/l, particularly preferably in each case at least 0.2 g/l. A topping-up solution alternatively can contain in particular chlorate,



peroxide or/and zinc. The concentrate is preferably diluted with water by a factor of 2 to 20 in order to prepare the bath solution.

[00109] It was surprising that it was possible to establish an extremely fine-grained phosphate layer by the addition of nitroguanidine. It was moreover surprising that it was possible to reduce the ratio of pickling erosion on the metallic surface to the layer weight of the phosphate layer to values down to about 47%, which were otherwise of the order of about 80% or even of about 110% and cause a correspondingly higher consumption of phosphate solution. It was possible by this means to reduce the consumption by a factor of up to about 3. It was furthermore surprising that by the addition of nitroguanidine in the presence of alkaline earth metal ions, in some cases a sludge which is significantly better to handle was formed. The addition of nitroguanidine here surprisingly eliminated the adverse effects of chloride, which occur in some cases, of possibly increasing the pickling attack and therefore increasing the sludge content and the consumption. Surprisingly, it was possible for the amount of sludge formed to be decreased to values of 10 to 50 wt.% of other phosphating processes according to the prior art which are employed for cold shaping. It was moreover surprising that it was possible, by the addition of nitroguanidine, to establish a wide operating range for stable phosphating conditions. It was furthermore surprising that by carrying out an activation beforehand, it was in some cases possible to establish certain layer weights of the phosphate layer in a targeted manner.

[00110] It seems here to have been possible for the first time to have found a phosphating which can be employed particularly advantageously industrially with only low additions, if at all, of nitrate or/and nitrite, and at the same time renders very small phosphate crystals possible.

[00111] Finally, it seems to have been possible for the first time to propose a phosphating which for the first time renders possible only a small amount of precipitated sludge during the formation of closed phosphate layers.

[00112] Examples and comparison examples:

[00113] The examples described in the following are intended to illustrate the subject matter of the invention in more detail without limiting it.

[00114] In a first series of experiments, steel sheets of cold-rolled steel (CRS), welded pipes of steel and slugs of carbon-containing steel of 90 to 120 HB 2.5/187.5 Brinell hardness were subjected to strongly alkaline cleaning, rinsed with cold water, activated with a titanium-containing activating agent and then coated at 70°C in the phosphating bath. The nitrate- and nitrite-free phosphating bath was prepared with the following initial composition, based on water:

[00115] 20.0 g/l of phosphate, calculated as  $\text{PO}_4$ ,

[00116] 3.5 g/l of zinc ions,

[00117] 0.3 g/l of calcium ions,

[00118] 0.6 g/l of magnesium ions,

[00119] 0.3 g/l of sodium ions,

[00120] 0 – 4.0 g/l of nitroguanidine,

[00121] 1.0 g/l of chlorate ions,

[00122] 0.9 g/l of chloride ions and

[00123] 0.5 g/l of fluoroborate.

[00124] No other N compound apart from nitroguanidine was added. The bath was immediately ready to use.

[00125] In a first series of experiments the influence of the nitroguanidine content of the phosphating bath with the abovementioned initial composition on the bath properties and the properties of the coating was determined.

[00126] Table 1: Properties of the bath and of the phosphate layer as a function of the nitroguanidine addition on CRS steel sheets and pipes and slugs

Example	CE 0	E 1	E 2	E 3	E 4	E 5
Nitroguanidine addition, g/l	0	0.3	0.5	1	2	4
Pickling erosion, g/m <sup>2</sup>	4.7	3.5	2.7	2.4	2.0	2.0
Consumption of the phosphating solution	c. 20%, >> A	n.d. <sup>1</sup>	n.d.	A	n.d.	n.d.
Sludge volume, ml/l	250	n.d.	n.d.	70	n.d.	n.d.
Sludge quality	hard	medium-hard	soft	soft	soft	soft
Layer weight, g/m <sup>2</sup>	9.0	6.8	4.7	3.8	2.8	2.7
Pickling erosion: layer weight in %	52.2	51.5	57.5	63.2	71.4	74.1
Average crystal size, µm	c. 60	c. 20	c. 2	c. 3.5	c. 3.5	c. 5
Shaping properties after coating with Na soap	poor	good	very good	very good	very good	very good

[00127] The sludge volume was determined at a throughput of 30 normal units NU (1 NU = 0.04 m<sup>2</sup>/l) of coated metallic surface. The sludge was deposited particularly solidly on heaters, especially in the case of no or only a low nitroguanidine content, but was nevertheless - regardless of the nitroguanidine content always - easy to rinse off. The layer weight was determined via detachment of the layer and the difference in weight beforehand and afterwards. The average crystal size was estimated on scanning electron microscope photographs perpendicular to the phosphate layer. The shaping properties were tested on pipes and slugs. For this, the phosphated bodies to be shaped were additionally coated in the conventional manner with a commercially available soap such as is employed for cold shaping. Without an addition of nitroguanidine the phosphate crystals of the phosphate layer became so large that the shaping properties worsened significantly in comparison with the examples according to the invention. The content of dissolved Fe<sup>2+</sup> in the phosphating bath, which was approximately zero at the start of the operation, rose here to values of about 1 g/l during more prolonged operation.

[00128] Such good phosphating properties and such good layer properties are unknown to the Applicant in phosphating processes according to the prior art for cold shaping, since to the knowledge of the Applicant finely crystalline phosphate layers of far less than 50 µm average phosphate crystal edge length with less than

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<sup>1</sup> Not determined

75% pickling erosion of the layer weight do not belong to the prior art, where e.g. 100 to 120% pickling erosion of the layer weight are usual according to the prior art in chlorate phosphating processes or 75 to 100% pickling erosion in nitrite-containing phosphating processes; the layer weight according to the prior art is conventionally in the range from 4 to 12 g/m<sup>2</sup> here.

[00129] In a second series of experiments the minimum phosphating time for a closed phosphate layer was determined. A bath of the initial composition with 0.5 g/l or 1 g/l of nitroguanidine was employed for this at 70°C after a titanium-containing activation.

[00130] Table 2: Determination of the layer weights according to the phosphating time and nitroguanidine content of the phosphating bath on steel sheets of CRS

Phosphating time, min	3	5	7	10
Layer weight at 0.5 g/l nitrog., g/m <sup>2</sup>	4.1	5.8	7.5	7.8
Layer weight at 1.0 g/l nitrog., g/m <sup>2</sup>	4.4	4.7	5.0	5.0
Closed layer at 0.5 g/l nitrog.	no	yes	yes	yes

[00131] The formation of the layer was checked on scanning electron microscope photographs. The phosphate layer of the bath with 0.5 or 1 g/l of nitroguanidine was closed after 5 minutes. In a phosphating bath without an addition of nitroguanidine, only virtually closed layers resulted after a phosphating time of 7 minutes.

[00132] In a third series of experiments the phosphating properties of a bath with the abovementioned initial composition were determined on rolled wires of steel with a content of 0.7 wt.% carbon. The wires were subjected to strongly alkaline cleaning, rinsed in water, pickled to remove rust in 15 per cent hydrochloric acid at room temperature for 5 to 10 minutes, depending on the degree of rusting, until free from rust deposits, rinsed again in water and pretreated with a titanium-containing activating agent, before the rolled wires were phosphated.

[00133] Table 3: Properties of the bath and of the phosphate layer as a function of the nitroguanidine addition on rolled wires

Example	CE 10	E 11	E 12	E 13	E 14	E 15
Nitroguanidine addition, g/l	0	0.3	0.5	1	2	4
Pickling erosion, g/m <sup>2</sup>	4.2	4.0	3.9	3.9	2.7	2.8
Layer weight, g/m <sup>2</sup>	6.4	6.3	6.9	6.8	4.8	4.4
Pickling erosion : layer weight in %	65.6	63.5	56.5	57.4	56.3	63.6

[00134] Because of the different rust content of the rolled wires and because of the different pickling times, relatively wide variations resulted in the measurement results. On the basis of the increased pickling erosion with the phosphating bath without a nitroguanidine content, a significantly higher sludge volume is to be expected than in the presence of nitroguanidine, since the sludge volume is proportional to the pickling erosion. In this series of experiments also, significantly better properties of the nitroguanidine-containing phosphating baths result compared with the nitroguanidine-free bath.

[00135] In a fourth and fifth series of experiments, steel sheets of cold-rolled steel (CRS) were subjected to strongly alkaline cleaning, rinsed with cold water, activated with a titanium-containing activating agent and then coated in the phosphating bath at 70°C. The phosphating bath A) or B) was prepared with the following initial composition, based on water:

[00136] A) 24.0 g/l of phosphate, calculated as PO<sub>4</sub>,

[00137] 6.0 g/l of zinc ions,

[00138] 0.2 g/l of nickel ions,

[00139] 0 - 5 g/l of calcium ions,

[00140] 0.1 g/l of magnesium ions,

[00141] 3.9 g/l of sodium ions,

[00142] 1.0 g/l of nitroguanidine,

[00143] 0.4 g/l of nitrate ions,

- [00144] 0 g/l of nitrite ions,
- [00145] 6.0 g/l of chlorate ions,
- [00146] 0.4 - 0.9 g/l of chloride ions and
- [00147] 0.4 g/l of fluoroborate
- [00148] or
- [00149] B) 20.0 g/l of phosphate, calculated as  $\text{PO}_4$ ,
- [00150] 3.5 g/l of zinc ions,
- [00151] 0.3 g/l of calcium ions,
- [00152] 0.6 g/l of magnesium ions,
- [00153] 0.3 g/l of sodium ions,
- [00154] 1.0 g/l of nitroguanidine,
- [00155] 0 g/l of nitrate ions,
- [00156] 0 g/l of nitrite ions,
- [00157] 1 - 11 g/l of chlorate ions,
- [00158] 0.5 - 1.5 g/l of chloride ions and
- [00159] 0.5 g/l of fluoroborate.
- [00160] No other N compound apart from nitroguanidine and in A) also nitrate was added. The baths A) and B) were also immediately ready to use, which is not a matter of course with phosphating baths.
- [00161] Table 4: Properties of bath A) and B) and the phosphate layer as a function of the calcium and chlorate addition

Example	CE 16	E 17	E 18	CE 19	E 20	CE 21
Bath	A)	A)	A)	A)	B)	B)
Calcium content, g/l	0	0	1	5	0.3	0.3
Chlorate content, g/l	6	6	6	6	1.5	11
Nitroguanidine content, g/l	0	1	1	1	1	1
Pickling erosion, g/m <sup>2</sup>	1.9	1.7	1.8	3.4	1.5	3.2
Layer weight, g/m <sup>2</sup>	4.0	3.0	2.9	2.7	3.2	2.6
Pickling erosion : layer weight in %	47.5	56.7	62.0	126	46.9	123

[00162] In phosphating bath A) a low pickling erosion and a comparatively low layer weight indeed resulted in the fresh state of the calcium-free bath, which initially contained only 0.4 g/l of chloride, but without a content of nitroguanidine a voluminous sludge and a high sludge content were found. Over time, the chloride content increased somewhat because of the high chlorate addition. The pickling erosion and layer weight were also reduced. By the addition of nitroguanidine, the sludge volume was reduced, the phosphating bath became clearer and the average edge length of the phosphate crystals was reduced somewhat. By the addition of nitroguanidine and calcium chloride, the chloride content was increased significantly, the sludge was precipitated significantly more compactly, the sludge volume was therefore reduced significantly and the average edge length of the phosphate crystals was reduced to significantly below 5 µm. At the same time, however, the ratio of pickling erosion to layer weight increased to very high values because of the addition of calcium chloride instead of calcium hydroxide, since the chloride content here was increased too much compared with the initial bath composition.

[00163] An adverse ratio of pickling erosion to layer weight also resulted in phosphating bath B) in the fresh state of the bath, because the chlorate content chosen was too high. However, the phosphating bath B) could be employed well and with a favourable ratio of pickling erosion to layer weight at a chlorate content in the range from 0.2 to 6 g/l. A chlorate content in the range from 0.5 to 2 g/l was sufficient here, since it was possible easily to limit the iron content dissolved in the bath by this means. A somewhat higher chlorate content did not cause trouble, but was not necessary. It was therefore then also possible to keep the chloride content

of the bath correspondingly low, and with good activation and at a nitroguanidine content in the range from 0.2 to 1.8 g/l an average edge length of the phosphate crystals of less than 5  $\mu\text{m}$  almost always resulted. At a chlorate content of 11 g/l, the pickling erosion was higher than the layer weight and the phosphate layers were iridescent blue and very thin.

[00164] In a sixth series of experiments, steel sheets of cold-rolled steel (CRS) were subjected to strongly alkaline cleaning, rinsed with cold water, activated with a titanium-containing activating agent and then coated in a phosphating bath at 60 to 70°C by dipping for 5 to 10 minutes. The phosphating bath was prepared with the following initial composition, based on water:

- [00165] 20.0 g/l of phosphate, calculated as  $\text{PO}_4$ ,
- [00166] 4.0 g/l of zinc ions,
- [00167] 0 g/l of manganese ions,
- [00168] 0 g/l of nickel ions,
- [00169] 0.3 g/l of calcium ions,
- [00170] 0.6 g/l of magnesium ions,
- [00171] 1.6 g/l of sodium ions,
- [00172] 0 - 1 g/l of nitroguanidine,
- [00173] 0 g/l of nitrate ions,
- [00174] 0 g/l of nitrite ions,
- [00175] 0.5 - 1 g/l of chlorate ions,
- [00176] 0.1 - 2 g/l of chloride ions,
- [00177] 0.8 g/l of fluoroborate and
- [00178] 0.2 g/l of fluoride ions.



[00179] No other N compound apart from nitroguanidine was added. The bath was immediately ready to use. Without a nitroguanidine content phosphate layers with an average edge length of the phosphate crystals of more than 50  $\mu\text{m}$  resulted, at a layer weight of 8 to 10  $\text{g}/\text{m}^2$ . In contrast, solely by the addition of 0.3 to 1  $\text{g}/\text{l}$  of nitroguanidine it was possible to establish, at a layer weight which was varied in the range from 2 to 15  $\text{g}/\text{m}^2$ , phosphate layers with an average edge length of the phosphate crystals in the range from 2 to 10  $\mu\text{m}$ . Over a throughput of two to three days, the sludge volume was 50 to 100  $\text{mg}/\text{l}$ .

[00180] It was thus found that the process according to the invention is particularly advantageous, economical and very readily usable industrially. The process procedure was simple.